

Thin films of oxidic materials having a high dielectric constant

The present invention relates to a process for coating a
5 substrate by applying a finely divided, stable suspension of
crystalline oxide particles to the substrate, which, if
required, is to be heated, by coating, evaporating the
suspending medium and sintering at elevated temperatures.

10 Oxidic materials having a high dielectric constant, such as
barium titanate, strontium titanate, mixed titanates of barium
and strontium, lead zirconium titanates or strontium bismuth
tantalate, are used as dielectrics or ferroelectrics for memory
chips in microelectronics.

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These materials on a substrate act as a dielectric if they are
applied as a film in layer thicknesses of about 100 nm in
crystalline form. A thermal treatment at from 300 to 1000°C has
to be carried out for producing a film.

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It is known from Appl. Phys. A 69 (1999), 55-61 that such films
can be obtained for the ferroelectric material $\text{SrBi}_2\text{Ta}_2\text{O}_9$ after
mixing and calcining SrCO_3 with Bi_2O_3 and Ta_2O_5 and subsequent
sintering of compressed pellets by means of laser irradiation

25 (sputtering) on a substrate. The disadvantage of this process is
that the stoichiometry of the material may change during the
sputtering procedure and that the dielectric constant or the
permanent polarizability may thus be adversely affected.

30 It was an object of the present invention to remedy the
abovementioned disadvantages.

We have found that this object is achieved by a novel and
improved process for coating a substrate, wherein a finely
35 divided suspension of crystalline oxide particles is applied to
a substrate by coating, the suspending medium is evaporated and
the coating on the substrate is sintered.

The novel process can be carried out as follows:

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The oxide suspensions can be sprayed by a suitable apparatus,
such as a spray nozzle, onto a substrate which, if required, is
heated to such a high temperature that the suspending medium
evaporates. The evaporation can also be effected in a separate
45 step by subsequent heating. A homogeneous spray cone can be
achieved by coupling the spray nozzle(s) to an ultrasonic
oscillator or superposing an ultrasonic oscillation during the

metering or metering the suspension onto a suitably shaped ultrasonic oscillator. The spraying of the unheated or moderately heated (temperature from room temperature to below the boiling point of the suspending medium) suspension can be
5 achieved in a binary nozzle by means of an auxiliary gas (for example nitrogen or argon) and/or by supporting the spray process, for example, by superposed ultrasonic oscillations.

The coating can be by spraying on or by a spin-on process in which
10 a certain amount of flowable suspension is metered at any desired point, for example in the center, of a rotating substrate and the suspension is distributed uniformly over the substrate as a result of the centrifugal force.

15 After deposition of the oxide suspension on the substrate is complete, the system can be heated to the crystallization temperature adequate for the oxide and the desired cohesive film can be produced by sintering together the nanoparticles.

20 The sintering temperatures for the nanoparticles are as a rule substantially below the sintering temperature for the particles on the micrometer scale. For example, for BaTiO_3 particles, the sintering temperature is about 750°C in the case of nanoparticles (particle sizes from 2 to 5 nm), in contrast to
25 micrometer particles (particle sizes from 2 to 5 μm), for which it is about 1350°C .

There is no change in the stoichiometry of the applied oxides, as occurs in the case of other processes. Thus, films having
30 superior dielectric or ferroelectric properties are obtained.

In the case of the suspensions of finely divided, crystalline oxide particles, as a rule water or organic suspending media are used, which contain the oxide particles with a mean particle
35 sizes of from 0.5 to 9.9 nm, preferably from 0.6 to 9 nm, particularly preferably from 1 to 8 nm. The oxide particles are, for example, BaTiO_3 , SrTiO_3 , $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ where $x = 0.01$ to 0.99, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ where $x = 0.01$ to 0.99, $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ where $x = 0$ to 4 or $\text{Sr Bi}_2\text{Ta}_2\text{O}_9$.

40 Suitable substrates are as a rule ultrapure silicon wafers which are already structured, the structuring being effected by the known damascene process. The actual substrate layers are electrically conductive layers which are produced in the course
45 of the damascene process.

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Suitable organic suspending media are as a rule polar organic suspending media, in particular aliphatic alcohols, ether alcohols or mixtures thereof, having a boiling point below about 300°C under atmospheric pressure. These can be used in anhydrous form or, preferably, in commercial aqueous form.

Suitable alcohols are C₁- to C₈-alkanols, preferably C₁- to C₄-alkanols, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol or tert-butanol, particularly preferably C₁- to C₃-alkanols, such as methanol, ethanol, n-propanol or isopropanol, in particular methanol or ethanol.

Suitable ether alcohols are all known glycol ethers, for example ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol monoisopropyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol monoisobutyl ether, ethylene glycol mono-sec-butyl ether, ethylene glycol tert-butyl ether, diethylene glycol dimethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol monoisopropyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol monoisobutyl ether, diethylene glycol mono-sec-butyl ether, or diethylene glycol tert-butyl ether, preferably ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol monoisopropyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol monoisobutyl ether, ethylene glycol mono-sec-butyl ether, ethylene glycol tert-butyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol monoisopropyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol monoisobutyl ether, diethylene glycol mono-sec-butyl ether and diethylene glycol tert-butyl ether, particularly preferably ethylene glycol mono-n-propyl ether, ethylene glycol monoisopropyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol monoisobutyl ether, ethylene glycol tert-butyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol monoisopropyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol monoisobutyl ether, diethylene glycol mono-sec-butyl ether and diethylene glycol tert-butyl ether, in particular ethylene glycol monoisopropyl ether, ethylene glycol monoisobutyl ether, ethylene glycol tert-butyl ether, diethylene glycol monoisopropyl ether, diethylene glycol monoisobutyl ether and diethylene glycol tert-butyl ether.

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The solids content of the suspensions can be varied within wide limits, is as a rule from 1 to 35, preferably from 5 to 25, % by weight and can be established in the synthesis of the suspensions or subsequently by dilution or concentration.

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The nanocrystalline oxide suspensions can be prepared as follows:

Titanium alcoholates in an alkanol, a glycol ether or a mixture thereof can be initially taken and reacted at from 50 to 150°C, preferably from 60 to 120°C, particularly preferably from 70 to 110°C, in particular at reflux temperature, and from 0.1 to 3, preferably from 0.5 to 2, bar, particularly preferably at atmospheric pressure, with barium hydroxide hydrate or strontium hydroxide hydrate.

The concentration of the alcoholic titanium alcoholate solution can be varied within wide limits. The concentration is preferably from 50 to 800, particularly preferably from 100 to 600, very particularly preferably from 200 to 400, g/liter.

Suitable barium hydroxide hydrates or strontium hydroxide hydrates are the known hydroxide hydrates, e.g. barium hydroxide octahydrate or strontium hydroxide octahydrate.

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Suitable titanium alcoholates are, for example, titanium tetramethanolate, titanium tetraethanolate, titanium tetra-n-propanolate, titanium tetraisopropanolate, titanium tetra-n-butanolate, titanium tetraisobutanolate, titanium tetra-sec-butanolate, titanium tetra-tert-butanolate, titanium tetra-n-pentanolate and titanium tetraisopentanolate, preferably titanium tetraethanolate, titanium tetra-n-propanolate, titanium butanolate, titanium tetra-sec-butanolate and titanium tetra-tert-butanolate, particularly preferably titanium tetra-n-propanolate, titanium tetraisopropanolate, titanium tetra-n-butanolate and titanium tetraisobutanolate, or mixtures thereof.

For the preparation of $\text{Ba}(\text{Zr}_x \text{Ti}_{1-x})\text{O}_3$ or $\text{Sr}(\text{Zr}_x \text{Ti}_{1-x})\text{O}_3$ oxides, the mixtures with zirconium alkoxides are used instead of the pure titanium alkoxide and the conditions described above are used.

Zirconium alkoxides used are the commercially available alkoxides, preferably zirconium tetraisobutanolate and/or zirconium tetra-n-butanolate.

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For the preparation of the $\text{Pb}(\text{Zr}_x \text{Ti}_{1-x})\text{O}_3$ oxides, the lead component used is as a rule lead acetate trihydrate or a mixture thereof with the basic lead acetate $[\text{Pb}(\text{OAc})_2 \cdot \text{Pb}(\text{OH})_2]$. By means of the mixing ratio of lead acetate trihydrate and basic lead acetate, the amount of the water of reaction can be predetermined, the acetate radicals being eliminated as acetic acid and the latter producing further water by ester formation with the alcohol present as component in the suspending medium. The addition of small amounts of additional acetic acid with formation of water of reaction may be advantageous.

For the preparation of $\text{SrBi}_2\text{Ta}_2\text{O}_9$, the alkoxide used is as a rule commercially available tantalum pentaethoxide $\text{Ta}(\text{OC}_2\text{H}_5)_5$ and the Sr component used is preferably $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, if required as a mixture with anhydrous $\text{Sr}(\text{OH})_2$, and the bismuth component used is $\text{Bi}(\text{OCOCH}_3)_3$ or bismuth hydroxide $\text{Bi}(\text{OH})_3$.

For the preparation of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$, the Li component used is as a rule nonaqueous lithium hydroxide, and the titanium component used is titanium alcoholates as listed above.

It may be advantageous to support the introduction of the solids by vigorous stirring.

An advantageous embodiment comprises introducing no additional water into the oxide suspensions in the reaction, apart from the water from the components and from the suspending medium.

If required, doping elements, such as Mg, Ca, Zn, Zr, V, Nb, Ta, Bi, Cr, Mo, W, Mn, Fe, Co, Ni, Pb, Ce or mixtures thereof, preferably Mg, Ca, Cr, Fe, Co, Ni, Pb or mixtures thereof, for example in the form of their hydroxides, oxides, carbonates, carboxylates or nitrates, may be introduced.

The mixed oxides prepared according to the invention have, as a rule, a mean particle diameter of less than 10 nm, preferably from 5 to 9.9 nm, particularly preferably from 0.6 to 9 nm, in particular from 1 to 8 nm.

By means of the novel process, it is possible to obtain dielectric layers for DRAMs (Dynamic Random Access Memories), for example titanates, BaTiO_3 , SrTiO_3 and $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (where $x = 0.01$ to 0.99), or ferroelectric layers for FeRAMs, for example $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ where $x = 0.01$ to 0.99 or $\text{SrBi}_2\text{Ta}_2\text{O}_9$ or $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ where $x = 0$ to 4 , for example $\text{Bi}_{3.15}\text{La}_{0.85}\text{Ti}_3\text{O}_{12}$

where $x = 0.85$, which lead to superior dielectric or ferroelectric properties without changing the stoichiometry.

Examples

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Example 1

Preparation of a nanoparticle barium titanate suspension

10 335.6 g of titanium tetrabutanolate and 79.6 g of $\text{Ba}(\text{OH})_2 \times 8\text{H}_2\text{O}$ with 128.4 g of $\text{Ba}(\text{OH})_2$ were added rapidly in succession to 844 g of butyl glycol and stirred for 48 hours at 120°C . A barium titanate suspensions highly crystalline particles having a mean particle size of from 4 to 6 nm was obtained.

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Example 2

Preparation of a nanoparticle $\text{SrBi}_2\text{Ta}_2\text{O}_9$ suspension of <10 nm

20 40.6 g of tantalum ethanolate, 4.6 g of $\text{Sr}(\text{OH})_2$ (Sr content: 70.4% by weight), 3.35 g of $\text{Sr}(\text{OH})_2 \times \text{H}_2\text{O}$ and 26 g of $\text{Bi}(\text{OH})_3$ were added in succession to 110 g of butyl glycol and stirred for 48 hours under reflux (104°C). A crystalline $\text{SrBi}_2\text{Ta}_2\text{O}_9$ suspension having a mean particle size of 5 nm was obtained.

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Example 3

Preparation of a nanoparticle $\text{SrBi}_2\text{Ta}_2\text{O}_9$ suspension of <10 nm

30 40.6 g of tantalum ethanolate, 1.55 g of $\text{Sr}(\text{OH})_2$ (Sr content: 70.4% by weight), 10 g of $\text{Sr}(\text{OH})_2 \times \text{H}_2\text{O}$ and 26 g of $\text{Bi}(\text{OH})_3$ were added in succession to 110 g of butyl glycol and stirred for 48 hours under reflux (104°C). A crystalline $\text{SrBi}_2\text{Ta}_2\text{O}_9$ suspension having a mean particle size of 8 nm was obtained.

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Example 4

Preparation of a nanoparticle $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ suspension

40 49.6 g of $\text{Zr}(\text{OC}_3\text{H}_7)_4$, 31.5 g of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and 75.8 g of $\text{Pb}(\text{OCOCH}_3)_2 \times 3\text{H}_2\text{O}$ were added in succession to 211 g of butyl glycol and stirred for 24 hours at 80°C and for 24 hours at 120°C . A crystalline $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ suspension having a mean particle size of from 2 to 3 nm was obtained.

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Example 5

Preparation of a nanoparticle $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ suspension

5 49.6 g of $\text{Zr}(\text{OC}_3\text{H}_7)_4$, 31.5 g of $\text{Ti}(\text{OC}_4\text{H}_9)_4$, 24 g of acetic acid
(100% strength) and 75.8 g of $\text{Pb}(\text{OCOCH}_3)_2 \times 3\text{H}_2\text{O}$ were added in
succession to 211 g of butyl glycol and stirred for 24 hours at
80°C and for 24 hours at 120°C. A crystalline $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$
suspension having a mean particle size of from 3 to 4 nm was
10 obtained.

Example 6

Preparation of a nanoparticle $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ suspension

15 48.5 g of $\text{Zr}(\text{OC}_4\text{H}_9)_4$, 31.5 g of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and 75.8 g of
 $\text{Pb}(\text{OCOCH}_3)_2 \times 3\text{H}_2\text{O}$ were added in succession to 211 g of butyl
glycol and stirred for 72 hours at 120°C. A crystalline
 $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ suspension having a mean particle size of from
20 2 to 3 nm was obtained.

Example 7

Preparation of a nanoparticle $\text{Bi}_{3.15}\text{La}_{0.85}\text{Ti}_3\text{O}_{12}$ suspension

25 33.5 g of $\text{Ti}(\text{OC}_4\text{H}_9)_4$, 27.3 g of $\text{Bi}(\text{OH})_3$, 5.4 g of $\text{La}(\text{OH})_3$ and
8 g of 100% strength acetic acid were added in succession to
110 g of butyl glycol and stirred for 48 h at 120°C. A
crystalline $\text{Bi}_{3.15}\text{La}_{0.85}\text{Ti}_3\text{O}_{12}$ suspension having a mean particle
30 size of from 2 to 4 nm was obtained.

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